

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

THIS PAGE BLANK (USPTO)

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 242 027
A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 87301324.7

(91) Int. Cl.4: **C08G 63/00** , **C08G 63/40** ,
C08G 63/68

(22) Date of filing: 16.02.87

(30) Priority: 15.02.86 JP 31612/86
21.02.86 JP 37718/86

(43) Date of publication of application:
21.10.87 Bulletin 87/43

(84) Designated Contracting States:
DE FR GB IT SE

(71) Applicant: Takemoto Yushi Kabushiki Kaisha
2-5, Minato-machi
Gamagouri-shi Aichi-ken(JP)

(72) Inventor: Kinoshita, Mitsuo
5-8 Nishikata Agehama Mito-cho
Hoi-gun Aichi-ken(JP)
Inventor: Imamura, Shigeru
4-68-12 Mori
Toyokawa-shi Aichi-ken(JP)
Inventor: Matsueda, Hirokazu
4-3-8 Nishiodakano
Toyohashi-shi Aichi-ken(JP)

(74) Representative: Ablewhite, Alan James et al
MARKS & CLERK 57/60 Lincoln's Inn Fields
London WC2A 3LS(GB)

(54) Block copolymers comprising rubber and polyester segments, method of preparation.

(57) Block copolymers comprising a liquid rubber component substituted by at least one polyester grouping, and functional derivatives thereof are advantageous additives for synthetic resins. A method for the production of the said copolymers comprises reacting a liquid rubber having one or more reactive hydrogen atoms within its molecule with at least one organic dicarboxylic anhydride and one or more species of 1,2-epoxide in the presence of catalyst.

EP 0 242 027 A2

NOVEL POLYMERS

The present invention relates to [liquid rubber]/[polyester] block copolymers (hereinafter referred to as PD-PES block copolymers), to methods for their manufacture, and to their use as additives for synthetic resins and more particularly as additives for thermosetting or thermoplastic synthetic resins.

Liquid rubber compounds including diene homopolymers, such as polybutadiene, polyisoprene and polychloroprene, and copolymers partially consisting of vinyl compounds, are widely used as rubber-like elastic substances in their own right, and are also used as additives for many kinds of thermosetting and thermoplastic resins to improve impact strength, add flexibility, prevent moulding shrinkage and cracks and improve adhesive and water resisting properties. They may also be used as reforming agents for other polymers.

Thermoplastic polyesters obtained by polycondensation of aliphatic dibasic acids, aromatic dibasic acids and alicyclic dibasic acids with aliphatic dihydric alcohols provide examples of polyester-type polymers.

Thermosetting and thermoplastic synthetic resins have a wide range of uses as domestic building materials, such as for bath tubs and purification tanks, as industrial materials such as for machines and electrical products, as materials for vehicles such as automobiles and railroad wagons and as storage tanks and containers, and it is common practice to add to these resins other types of synthetic resins, fillers, fibre-reinforcing materials, etc to improve physical characteristics such as mechanical strength. It is particularly important to maximise impact strength when the product is used for construction purposes. Thus, rubber materials and other polymers, in addition to many other kinds of reinforcing materials, have been used as additives for synthetic resins, depending on the purpose for which the resin is intended.

Polyesters obtained from aromatic dicarboxylic acids or butyl glycol are employed for their superior properties as materials for synthetic fibres, moulded synthetic resin products, films, sheets and coating materials. Unsaturated polyesters containing α,β -unsaturated dicarboxylic acids as the dibasic acid constituent also find wide industrial application.

Although liquid rubber compounds and polyester-type polymers are both widely used in broadly similar applications, there are significant differences between them in both their physical and other characteristics, and polymers having the characteristics of both would be of tremendous value.

The volume of thermosetting synthetic resins usually reduces by between 7-10% during setting, so the external appearance and the accuracy in measurements of the finished products is adversely affected. In attempts to counteract this effect, rubber materials and other thermoplastic synthetic resins have been blended with the precursor unsaturated polyesters. Among the rubber materials used for improving impact strength and reducing mould shrinkage are polybutadienes, butadiene-styrene copolymers, butadiene-acrylonitrile copolymers, butadiene-styrene-acrylonitrile copolymers and modified polybutadienes.

Synthetic resins principally used to produce reinforced plastics with improved impact strength are commonly known as matrix resins. Thermosetting unsaturated polyester resins and thermoplastic resins such as polyethylene terephthalate, polybutylene terephthalate, polycarbonate and polyamide are widely used as matrix resins, as they possess superior thermal stability, light resistance, moulding characteristics and mechanical properties. Such resins are reinforced by adding, for example, any of the following: a rubber-type substance, a reinforcing material, a pigment, a filler, and by using many different kinds of moulding process.

Matrix resins and rubber materials vary considerably in physical characteristics such as polarity and solubility, and it is extremely difficult to obtain a uniform mix or to disperse them stably. Moulded products obtained from an unstable mixture tend to have a blemished finish. The surface has indentations and protrusions and rubber materials may appear on the surface. Mechanical strength is reduced and shrinkage unaffected. Furthermore, one of the components may coagulate at the time of moulding, affecting the moulding characteristics and increasing fluctuations in the physical characteristics of the product.

Thus, there is a need to develop additives which can mix uniformly with, and stably disperse in, thermosetting or thermoplastic matrix resins, and should be able to both enhance moulding characteristics, so products with a good finish can be manufactured, increase the mechanical strength of the products and reduce shrinkage.

Many ideas have been tested to improve compatibility and/or dispersibility with thermosetting or thermoplastic synthetic resins. For example, to improve moulding, the rubber material has been graft-polymerised with another monomer such as styrene, maleic acid, methacrylates, acrylates, etc. (Japanese Patent Publications Tokkai 54-18862 and 54-40846). However, graft efficiency is not high and the compatibility and dispersibility are not satisfactorily high. To improve compatibility with thermosetting synthetic

resins, styrene-type block copolymers have been considered (Japanese Patent Publications Tokkai 53-74592 and 60-99158). Compatibility is improved to a certain extent by the methods in these publications, but suffer, from the point of view of shrinkage and impact strength, as the styrene-type polymers used basically lack strength. Rubber modification of unsaturated polyester resins has also been tried using, for example, the Diels-Alder addition reaction to conjugate diene products such as dicyclopentadiene to the double bond of an unsaturated polyester having an α,β -unsaturated dicarboxylic acid moiety (Japanese Patent Publication Tokkai 58-2315). Again improved compatibility is observed with unsaturated polyester resins as the amount of conjugate diene-type products added is small, but the method is not effective in reducing shrinkage or increasing impact strength.

It is therefore an object of the present invention to provide both rubber/polyester compounds, possessing properties of both components, and copolymers as additives for synthetic resins which can overcome the above problems and satisfy the stated requirements.

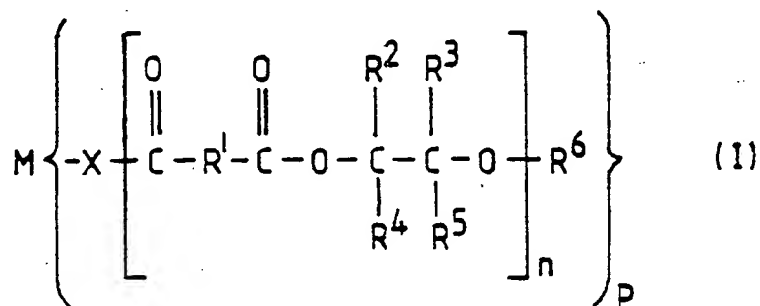
It has now been discovered that PD-PES block copolymers comprising a liquid rubber and a polyester satisfy both objects.

The new copolymers have the characteristics of either liquid rubber-type compounds or polyester-type polymers or both, and comprise conjugates of the two types of molecule. Previous attempts at producing such copolymers involved polycondensation of liquid rubber-type compounds with dibasic acid and aliphatic dihydric alcohol, or combining liquid rubber-type compounds with polyester-type polymers, either directly or by using a bridge-forming agent. By-products of unknown structure are generated by such methods and so are unsatisfactory for industrial use.

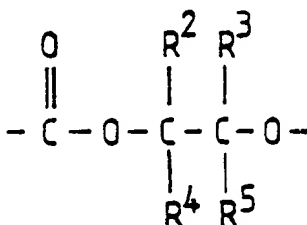
Thus, in a first aspect of the present invention there is provided a block copolymer comprising a liquid rubber substituted with at least one polyester grouping.

As used herein "liquid rubber" means non-crosslinked rubber. It can be natural or synthetic and is preferably polydiene, most preferably a homopolymer such as poly-1,2-butadiene or polyisoprene. The individual diene monomers are preferably in the *cis* conformation.

In a further aspect of the present invention there is provided a block copolymer of formula (I):



wherein M is substantially all or part of a molecule of a liquid rubber;
X is oxygen, sulphur, imino, amino, C_{1-8} alkyl-substituted amino or the group



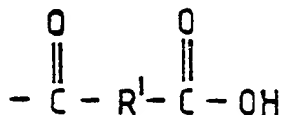
wherein R^2 - R^5 are as defined below;

R^1 is a C_{1-8} straight, branched or cyclo-alkylene or C_{2-8} straight, branched or cyclo-alkenylene, optionally substituted by hydroxy, amino, C_{1-4} alkyl, C_{1-4} alkoxy or any combination thereof, or is a C_{6-10} delocalised ring system, optionally substituted as above, and is the same or different in each repeat unit;

R^2 - R^5 are the same or different and are hydrogen or C_{1-4} alkyl and are the same or different in each repeat unit;

n and p are positive integers;

R¹ is hydrogen or



wherein R¹ is as defined and functional derivatives thereof.

In an alternative aspect of the present invention, there are provided additives for synthetic resins comprising [liquid rubber]/[polyester] block copolymers having a liquid rubber portion and a polyester portion blocked together such that in each copolymer one or more polyester molecules are linked through ester bonds to each liquid rubber molecule.

The PD-PES block copolymers of this invention can be produced stably in an industrially advantageous manner by starting with a liquid rubber compound having within its molecule a grouping with a reactive hydrogen, such as hydroxyl group, a thiol group, a primary or secondary amino group, an imino group or a carboxyl group, and polycondensing organic dicarboxylic anhydride and 1,2-epoxide with it in the presence of a catalyst to introduce a polyester chain at the reactive group of the liquid rubber. The polyester chain is formed, as a hydroxyl group is regenerated with each ring opening addition of a 1,2-epoxide to the carboxyl formed every time on organic dicarboxylic anhydride reacts with a hydroxyl group. A further anhydride then adds to the new hydroxyl and the process repeated. Thus, the polyester chain is formed by an esterification reaction between an hydroxyl group and an organic dicarboxylic anhydride taking place alternatively and sequentially.

When the active group is carboxyl then, if n moles of organic dicarboxylic anhydride are used for each carboxyl group, the amount of epoxide used is between n and n+1 moles (where n is greater than 1). In the case where the active hydrogen group is other than carboxyl, then the amount of anhydride used if n moles of epoxide are used for each active hydrogen group is between n and n+1 moles.

It will be appreciated that, in the instance where the reactive hydrogen group is carboxyl, the first step in polymer formation is the addition of epoxide, not anhydride.

The present invention thus further provides a method for the production of liquid rubber polyester block copolymers comprising reaction of a liquid rubber-type compound having one or more active hydrogen atoms with at least one organic dicarboxylic anhydride and one or more species of 1,2-epoxide in the presence of a catalyst.

The liquid rubber compounds which may be used in the aforementioned process include diene homopolymers having a suitable active hydrogen group such as a hydroxyl, thiol, primary or secondary amino, or carboxyl group as mentioned above, as well as those of the above partially containing, preferably in very small quantities, a vinyl-type compound. The active hydrogen group or groups may be either along the length of a polydiene chain or at its ends. The positions in the polydiene chain at which such active hydrogen groups are introduced are not essential and do not limit the present invention; nor is the present invention limited with respect to stereoisomers and structural isomers of the polymers or by the polymerization method such as radical polymerization, anion polymerization and anion "living" polymerization. Monomer diene compounds preferred for use as described above include butadiene, isoprene, chloroprene, 1,3-pentadiene and cyclopentadiene.

Particular examples of liquid rubber compounds which may be used advantageously in the aforementioned reaction include α,ω -poly-1,2-butadiene glycol (Nisso PB-G series), α,ω -poly-1,2-butadiene carboxylic acid (Nisso PB-C series), α,ω -poly-1,2-butadiene glycol mono-malate (Nisso PB-GM series, the above three produced by Nippon Soda, Inc.), end carboxyl modified poly-1,4-butadiene (Hycar CTB series produced by Ube Kosan, Inc. or B.F. Goodrich, Inc.) and end hydroxyl modified poly-1,4-butadiene (Poly-bd R-45M or R-45HT produced by Idemitsu Sekiyu Kagaku, Inc. or Arco Chemical, Inc.). Any of the aforementioned liquid rubber compounds hydrogenated either partially or completely to the carbon-carbon double bond in its principal or side chain provides a suitable liquid rubber compound having active hydrogen group. Examples include hydrogenated α,ω -poly-1,2-butadiene glycol (Nisso PB-GI series produced by Nippon Soda, Inc.) and hydrogenated α,ω -poly-1,2-butadiene dicarboxylic acid (Nisso PB-CI series produced by Nippon Soda, Inc.).

Examples of organic dicarboxylic anhydride for use in the aforementioned reaction include aliphatic dicarboxylic anhydrides such as succinic anhydride, maleic anhydride and alkenyl succinic anhydride, aromatic dicarboxylic anhydrides such as phthalic anhydride and naphthalene dicarboxylic anhydride and alicyclic dicarboxylic anhydride such as cyclohexane dicarboxylic anhydride, cyclohexene dicarboxylic anhydride.

Suitable examples of 1,2-epoxide include aliphatic epoxides such as ethylene oxide, propylene oxide, 1,2-butylene oxide and alkyl or alkenyl glycidylether with 1 to 12 carbon atoms, aromatic epoxides and alicyclic epoxides such as phenylene oxide and cyclohexane oxide, epoxides having an aromatic group such as styrene oxide and phenyl glycidylether and epoxides having an α , β -unsaturated hydrocarbon group such as glycidyl methacrylate and glycidyl acrylate. Examples of catalyst to be used in the
 5 aforementioned reaction include lithium halides such as lithium chloride and lithium bromide and tetra C₁-alkyl quaternary ammonium salts such as tetramethyl ammonium bromide, tributylmethyl ammonium bromide, and tetrapropyl ammonium chloride.

In a preferred embodiment, a PD-PES block copolymer of the present invention is prepared as follows.
 10 In either the presence or absence of inactive solvent, predetermined amounts of anhydride and catalyst per mole of liquid rubber are placed inside a reaction vessel and a predetermined amount of epoxide is introduced under atmospheric or elevated pressure. The mixture is caused to react at 50-200°C, preferably between 120-150°C, to obtain a PD-PES block polymer.

The end groups of the polyester chains in the block copolymers of the present invention are usually
 15 hydroxyl groups or carboxyl groups, or a mixture thereof. The exact ratio depends on the molar ratio between anhydride and epoxide used. Thus, the ratio between hydroxyl and carboxyl end groups can be selected by varying the ratio between the reactants.

The aforementioned hydroxyl and/or carboxyl end groups may be further modified by reaction with various compounds having reactive groups such as vinyl, epoxy, and isocyanate groups. These add through
 20 bonds such as ether and ester linkages, contributing to end modifications. Specific end-carboxyl groups may be generated by the reaction of dicarboxylic acids, polybasic acids (bivalent or greater) or their anhydrides, with an end hydroxyl group. The end groups may be blocked using, for example, ether, ester or amide bonds. Salts of alkali, or alkaline earth, metals may be used to inactivate end-carboxyls.

Magnesium oxide and isocyanate end-group modifications may be used for increasing viscosity for
 25 sheet moulding components (SMC) and bulk moulding compounds (BMC). For added stability when using unsaturated polyester resin premixes as moulding materials, and to improve physical characteristics of the moulded products, the ratio of carboxyl end groups is preferably greater when magnesium oxide is used, and the ratio of hydroxyl end groups is preferably greater when di-isocyanates are used.

PD-PES block copolymers with reactive end modifications as described above are useful as additives to
 30 improve the physical characteristics of the moulded products, as chemical bonds may be formed between the reactive groups and the matrix resins or various fillers and crosslinking agents. Those with inactive end modifications are useful in improving compatibility with matrix resins or for chemical stability.

The PD-PES block copolymers of the present invention have particularly superior characteristics as additives for improving impact strength and/or reducing shrinkage of moulded products using thermosetting
 35 resins and various thermoplastic resins as matrix resin. This is due to their more uniform and stable compatibility and dispersibility with matrix resins compared with the rubber-like substances and thermoplastic resins which have been used conventionally for similar purposes. PD-PES block copolymers with the desired characteristics can be obtained by varying the molecular weights, structures and compositions of their liquid rubber and polyester parts as well as the ratio between their molecular weights. Compatibility
 40 and dispersibility with matrix resins can be improved generally by increasing the molecular weight of the polyester part relative to the liquid rubber compound part. More particularly, desired characteristics can be achieved by appropriate variation of the types of anhydride and epoxide monomer constituting the polyester portion, as well as the ratio therebetween, depending on the type of matrix resin. Increasing the ratio of polyester does not necessarily improve the surface characteristics of the moulded products, but it does
 45 improve compatibility with matrix resins. To improve both compatibility/dispersibility and the surface characteristics of the moulded products, therefore, the ratio between liquid rubber and the polyester is critical. The ratio in each case will be determined by the structure of each polymer and the matrix resin used.

The ratio of rubber to polyester determines the amphipathic property of the block copolymer with
 50 respect to rubber-type and polyester-type substances. If the ratio of polyester to liquid rubber is relatively low, the polyester-type qualities tend to be swamped. This can be altered/reversed by increasing the ratio. The amphipathic property of block copolymers according to the present invention is exhibited when the ratio of the liquid rubber component to the total block copolymer is in the range of 95-5 weight %. In any event, the length of the polyester chain in the block copolymer can be accurately determined.

Another important factor controlling the physical properties of the block copolymers according to the present invention is the structure and composition of the polymers from which they are formed. Physical characteristics of a block copolymer are greatly influenced by the properties of its individual components, while the physical characteristics of the individual components are dependent on their constituent monomers. Thus, the physical characteristics of the copolymer and its rubber and polyester components, such as melting points, softening points and glass transition points can be modified by appropriate selection of monomers.

When the PD-PES block copolymers of the present invention are used as an additive for the purpose of improving impact strength and reducing shrinkage at the time of moulding, therefore, it is advantageous that the ratio between the liquid rubber compound part is between 10 and 95 weight %. It is particularly advantageous that this ratio be between 40 and 90 weight % for use with thermosetting synthetic resins. If the ratio of polyester part is less than 5 weight %, dispersibility with matrix resins is poor.

It will be appreciated that, while PD-PES block copolymers have been described as additives for matrix resins, they can also be used to advantage for stably dispersing other types of thermoplastic resin not compatible with matrix resins.

When used as additives, the PD-PES block copolymers of the present invention may also be mixed with appropriate amounts of elastomers or prepolymers (thermosetting synthetic resin materials), thermoplastic resins, monomers with vinyl polymerization characteristics, organic solvents, plasticisers, organic or inorganic bulk-increasing materials, fibre reinforcing materials, etc. When PD-PES block copolymers are used with thermosetting unsaturated polyester resins, in particular, it is advantageous to dilute them appropriately with a monomer with vinyl polymerization characteristics such as styrene, methyl styrene, methyl methacrylate, etc.

The following Examples serve to illustrate the present invention but are not intended to limit it in any way.

Section A

Test Example No. 1

In an autoclave were placed 222g (1.5 moles) of phthalic anhydride, 350g (3.5 moles) of succinic anhydride, 16340g (11.4 moles) of α , ω -poly-1,2-butadiene glycol (Nisson PB-G1000 produced by Nippon Soda, Inc. with average molecular weight of 1430) and 10g of lithium chloride. After nitrogen gas was substituted inside the reaction system, the mixture was stirred and heated to 130°C. Next, 290g (5 moles) of propylene oxide was compressed in over a period of 60 minutes at a temperature of 130-140°C. The reaction was complete after 2 hours under these conditions and 17185g of yellowish transparent viscous product was obtained.

The polybutadiene-polyester block copolymer thus obtained (Product A) had molecular weight of 1505, ratio of polydiene component 95.0%, acid value of 31 and hydroxyl group value of 46. As used herein, molecular weight is the calculated value and weight % is denoted as "%".

Test Example No. 2

The same materials and method were used as in Test Example No.1 but in the ratios shown in Table 1 to produce different polybutadiene-polyester block copolymers (Products B, C, D and E). Lithium bromide (0.7g) was used as catalyst.

TABLE 1

	Polybutadiene-Polyester Block Copolymer	B	C	D	E
5	(g)	715.0	715.0	715.0	715.0
	α, ω -Poly-1,2-butadiene Glycol				
10	(Mols)	0.5	0.5	0.5	0.5
<hr/>					
	(g)	52.3	88.8	176.6	355.2
15	Phthalic Anhydride				
	(Mols)	0.35	0.6	1.2	2.4
<hr/>					
	(g)	82.5	140.0	280.0	560.0
20	Succinic Anhydride				
	(Mols)	0.825	1.4	2.8	5.6
<hr/>					
	(g)	4.27	92.8	208.8	440.8
25	Propylene Oxide				
	(Mols)	0.74	1.6	3.6	7.6
<hr/>					
	Molecular Weight	1786.0	2073.0	2763.0	4142.0
30	Ratio of Polybutadiene (%)	80.0	69.0	51.8	34.5
	Acid Value	27.0	23.0	17.0	12.0
35	Hydroxyl Group Value	38.0	32.0	25.0	16.0

Test Example No.3

40 In an autoclave were placed 130.2g (1.3 moles) of succinic anhydride, 105.2g (0.71 moles) of phthalic anhydride, 35.8g (0.365 moles) of maleic anhydride, 1430g (1 mole) of α, ω -poly-1,2-butadiene glycol and 0.6g of lithium chloride. After nitrogen gas was substituted inside the reaction system, the mixture was stirred and heated to 130°C. Next, 86.3g (1.49 moles) of propylene oxide was compressed in over a period of 40 minutes at a temperature of 125-130°C. The reaction was complete after 2 hours under these conditions and a polybutadiene-polyester block copolymer was obtained. After the product was cooled, 447g of styrene monomer was added to form an 80% solution.

45 The polybutadiene-polyester block copolymer thus obtained had molecular weight of 1787 and ratio of polydiene component 80%. The acid value of this styrene solution was 25.6 and the hydroxyl group value was 26.3.

Test Example 4

55 In a flask were placed 800g (0.448 moles) of Product B and 54.2g (0.54 moles) of succinic anhydride. These were maintained at 120-125°C for 2 hours under a stream of nitrogen. After cooling to 50°C, 200g of styrene monomer was added to form a solution.

A polybutadiene-polyester block copolymer with carboxyl-modified ends of polyester chains was obtained. The acid value of the styrene solution was 50.7 and the hydroxyl group value was 1.9.

5 Test Example 5

In an autoclave were placed 175g (1.75 moles) of succinic anhydride, 111g (0.75 moles) of phthalic anhydride, 1520g (1 mole) of α,ω -poly-1,2-butadiene dicarboxylic acid (Nisso PB-C1000 produced by Nippon Soda, Inc. with average molecular weight of 1520) and 0.75g of lithium chloride. After nitrogen gas was substituted inside the reaction system, the mixture was stirred and heated to 135°C. Next, 210g (3.65 moles) of propylene oxide was compressed in over a period of 1 hour at a temperature of 135-145°C. The reaction was complete after 2 hours under these conditions, yielding 2016g of a yellowish transparent viscous product.

The polybutadiene-polyester block copolymer thus obtained had molecular weight of 2017, a ratio of polydiene component of 75.0%, an acid value of 36.1 and a hydroxyl group value of 39.1.

Test Example No. 6

In an autoclave were placed 135g (0.875 moles) of cyclohexane dicarboxylic anhydride (Rikacid produced by Shin Nippon Rika, Inc.), 56g (0.375 moles) of phthalic anhydride, 2400g (0.5 moles) of end carboxyl modified poly-1,4-butadiene (Hycar CTB produced by Ube Kosan, Inc. with average molecular weight of 48000) and 1.1g of lithium chloride. After nitrogen gas was substituted inside the reaction system, the mixture was stirred and heated to 135°C. Next, 106g (1.82 moles) of propylene oxide was compressed in over a period of 1.5 hours at a temperature of 135-145°C. The reaction was complete after 3 hours under these conditions and a polybutadiene-polyester block copolymer was obtained. After cooling, 1797g of styrene monomer was added to prepare 4493g of styrene solution containing the block copolymer.

The block copolymer thus obtained had a molecular weight of 5392 and a ratio of polydiene component of 89%. The acid value of this styrene solution was 19.5 and its hydroxyl group value was 45.6.

Test Example No. 7

In an autoclave were placed 123g (0.8 moles) of cyclohexane dicarboxylic anhydride, 30g (0.20 moles) of cyclohexene dicarboxylic anhydride (Rikacid TH produced by Shin Nippon Rika, Inc.), 37g (0.25 moles) of maleic anhydride acid, 1750g (0.5 moles) of end carboxyl modified poly-1,4-butadiene acrylonitrile block copolymer (Hycar CTBN produced by Ube Kosan, Inc. with average molecular weight of 3500 and containing 8 Mole % of acrylonitrile) and 1.2g of tetra-methyl ammonium bromide. Thereafter 80g (1.82 moles) of propylene oxide was compressed as described in Test Example No. 6 and 2018g of a yellowish transparent viscous product was obtained.

The block copolymer thus obtained had molecular weight of 4040, ratio of polydiene segment 86.6%, acid value of 35.3 and hydroxyl group value of 64.2

45 Comparison Test No.1

In a flask were placed 80g (1.05 moles) of propylene glycol and 350g (0.245 moles) of α,ω -poly-1,2-butadiene glycol and the mixture heated to 80°C with stirring and nitrogen gas was introduced into the reaction system. Thereafter, 91g (0.61 moles) of phthalic anhydride and 60g (0.61 moles) of maleic anhydride were added and the mixture further heated to gradually increase the temperature of the reacting system. An atmosphere of nitrogen was maintained. When the temperature of the reaction system reached 170°C, water began to be generated by dehydration and condensation. Heating was continued to complete esterification but the temperature of the reaction system increased suddenly. The contents gelled and could no longer be stirred. The desired product was not obtained.

Comparison Test No.2

Comparison Test No.1 was repeated with succinic anhydride instead of maleic anhydride. The result was the same as in Comparison Test No. 1 and the desired product was not obtained.

Comparison Test No.3

In a flask were placed 98g (1.0 mole) of maleic anhydride, 148g (1.0 mole) of phthalic anhydride and 159.6g (2.15 moles) of propylene glycol. The mixture was heated to 210-220°C and nitrogen gas introduced. The reaction was stopped when the acid value of the esterification condensate reached 25 and 365g of unsaturated polyester was obtained. Subsequently, 715g (0.5 moles) of α,ω -poly-1,2-butadiene glycol, 500m ω of xylene and 5 g of paratoluene sulfonic acid as catalyst were added for an esterification reaction with a xylene reflux until the effluence of water generated by the reaction stopped. After paratoluene sulfonic acid was neutralized with a water solution of sodium carbonate, xylene was distilled out under a reduced pressure to obtain the product.

The product thus obtained was separated into two layers, the upper layer containing about 350g of a mixture of which the principal constituent was unreacted α,ω -poly-1,2-butadiene glycol. The lower layer was used for evaluation and was a polybutadiene modified polyester.

Evaluation No.1

In a beaker were placed 60 parts by weight of styrene solution of unsaturated polyester resin containing 60% of solid components (Polyset 9107 produced by Hitachi Kasei, Inc.: Ester phthalate type), 27 weight parts of styrene monomer and 13 weight parts of additives shown in Table 2 and the contents stirred uniformly for 5 minutes by a propeller stirrer. The mixture was transferred to a 100-ml measuring cylinder, and left at room temperature with separation and changes with time being observed. The results are shown in Table 2.

TABLE 2

5

10

15

20

25

30

35

<u>Additive</u>	<u>Condition</u>		<u>After 20 Min.</u>	<u>After 1 Hr.</u>	<u>After 24 hrs.</u>
	<u>Immediately</u>	<u>After Stationary</u>			
A	White, turbid	dispersion	a	b	c
B	White, turbid-minute	dispersion	a	a	b
C	Minute dispersion		a	a	a
D	Becomes soluble		a	a	a
E	Uniform dissolution		a	a	a
PBG	Separation into	two layers	c	c	c
SBS	White, turbid-partial	separation	c	c	c
PES	White, turbid	dispersion	b	c	c
SES	White, turbid	dispersion	a-b	c	c

Note: A, B, C, D and E: As explained above

PBG: α,ω -poly-1,2-butadiene glycol

SBS: Styrene-butadiene-styrene block copolymer
(Cariflex TR1102 produced by Shell Chemicals, Inc.)

PES: Product obtained in Comparison Test No. 3.

SES: Block copolymer of styrene-type polymer obtained by suspension polymerization of styrene monomer and end modified polyester (Tokkai 60-9915)

a = Stable dispersion, no separation observed

b = Slight separation

c = Separation clearly observed.

50

Evaluation No. 2

In a 60 ml beaker were placed 90 parts by weight of liquid polybutadiene (Nisso PB B1000) and 10 parts of the additives shown in Table 3.

55

The mixtures were observed as described in Evaluation No.1. Results are shown in Table 3.

TABLE 3

5

10

	<u>Additive</u>	<u>Condition Immediately After Remaining Stationary</u>	<u>After</u>		
			<u>20 Min.</u>	<u>1 Hr.</u>	<u>24 hrs.</u>
15	A	Uniform dissolution	a	a	a
	B	Becomes Soluble	a	a	a
	C	Minute Dispersion	a	a	a
20	D	Minute-white, turbid dispersion	a	b	b
	E	White, turbid dispersion	a	b	c
25	UP	Separation into two layers	c	c	c
30	Modified UP	White, turbid dispersion-partial separation	c	c	c
	PES	White, turbid dispersion	b	c	c
35	SES	Separation into two layers	c	c	c

40

Note: A - E, PES, SES, Evaluation: as Evaluation No.1

UP: Styrene solution of unsaturated polyester resin containing 60% solid component (as used in Evaluation No. 1).

Modified UP: Cyclopentadiene graft modified unsaturated polyester (Tokkai 58-2315).

45

Evaluation No.3

Forty parts by weight, of 33% styrene solution of the additives in Table 4, 60 parts of unsaturated polyester resin (Polyset 9120 produced by Hitachi Kasei, Inc.), 3 parts of zinc stearate, 1.5 part of tertiary butyl perbenzoate, 140 parts of calcium carbonate powder and 0.3 parts of para-benzoquinone were all mixed. Subsequently, 2 parts of magnesium oxide were added to immediately yield a product containing 10% of glass fibr with a fibre length of 1 inch. This was poured into a mould and heated to a mould temperature of 140°C for forming. The SMC obtained was evaluated for lustre and rate of shrinkage. Results of the evaluation are shown in Table 4.

55

TABLE 4

5

10

15

20

25

30

35

40

45

50

55

<u>Additive</u>	<u>Lustre</u>	<u>Ratio of moulding shrinkage (%)</u>
A	b	-0.10
B	a-b	-0.07
C	a	-0.02
D	a	0.06
E	a	0.12
PBG	c	-0.20
PBA	c	-0.18
SES	b	0.25

Note: A-E, PBG, SES: as Evaluation No. 1.

PBA: α,ω -poly-1,2-butadiene dicarboxylic acid
(Nisso PB-C1000)

a = Lustre good

b = Lustre not very good

c = No Lustre

Evaluation No. 4

Polybutylene terephthalate resin (0.5% orthochlorophenol solution with relative viscosity 1.70 at 25°C) and the additives shown in Table 5 were mixed in a ratio of 90/10 (by weight) and pellets were formed using an extruder with a vent diameter of 40 mm for fusing and kneading. After the pellets were vacuum-dried, products were obtained by injection moulding. The Izod impact strength (with notches) of this product was measured (ASTM-D256-56). Results are shown in Table 5.

TABLE 5

<u>Additive</u>	<u>Izod Impact Strength</u> <u>(kg·cm/cm)</u>
A	7.9
B	8.4
C	8.2
D	7.5
E	6.8
PBA	2.5-3.2
SES	2.8
None	3.0

Note: A-E, PBA, SES: As Evaluation No. 1.

As will be seen from the above Test Examples and Evaluations, the present invention provides an industrially practicable method of producing block copolymers of consistent quality, having the characteristics of both liquid rubber-type compounds and polyester-type polymers and having affinity to either or both.

Section BProduction Example (No.1 B' in Table 1a below)

Inside an autoclave were placed 52.3g (0.35 moles) of phthalic anhydride, 82.5g (0.825 moles) of succinic anhydride, 0.7g of lithium chloride as catalyst and 715g (0.5 moles) of α,ω -poly-1,2-butadiene glycol (Nisso PB-G1000 with average molecular weight of 1430 produced by Nippon Soda, Inc.) and after nitrogen gas was introduced into the reacting system, the mixture was heated to 130°C with stirring. Next, 42.7g (0.74 moles) of propylene oxide was compressed in over a period of one hour. The reaction was complete after 2 hours at 130°C and 890g of yellowish transparent viscous product was obtained. The molecular weight of the polybutadiene-polyester block copolymer thus obtained was 1786, the ratio of its polydiene segment was 80.0 %, its acid value was 27 and its hydroxyl value was 38.

A yellowish transparent styrene solution containing 80% of block copolymer was obtained by adding 200g of styrene monomer of 0.1 g of hydroquinone to 800g of the block copolymer.

Production Example No.2 (J in Table 2a below)

Inside a flask were placed 800g (0.448 moles) of the block copolymer of Production Example No.1 described above and 54.2g (0.54 moles) of succinic anhydride for a reaction at 120-125°C for two hours in a nitrogen reflux. After the content was cooled to 50°C, it was dissolved by adding 200g of styrene monomer. The acid value of the styrene solution containing block copolymer was 50.7 and its hydroxyl value was 1.9. Polybutadiene-polyester block copolymer with carboxy-modified ends of polyester chains was obtained.

10

15

20

25

30

35

40

45

50

55

Test No. 1 (PD-PES block copolymers)

PD-PES block copolymers shown in Table 1a were obtained as described in Production Example No.1.

TABLE 1a

	Liquid Rubber Compound Molecular	Polyester Chain Forming Component	Molecular Wt of PD-PES Block Copolymer	Ratio of Polydiene Segment (%)	End Group Molar Ratio	
Kind	Wt					
		* 1	* 2			
		Molar Ratio				
A	* 3 1430	SA/PA 7/3	PO	1505	95.0	COOH/OH 40.3/59.7
B	Same as above	Same as above	Same as above	1786	80.0	Same as above 41.5/58.5
C	Same as above	Same as above	Same as above	2073	69.0	Same as above 41.8/58.2
D	Same as above	Same as above	Same as above	2763	51.8	Same as above 40.4/59.6
E	Same as above	Same as above	Same as above	4142	34.5	Same as above 42.9/57.1
F	Same as above	SP/PA/MA 5.5/3.0/1.5	Same as above	1786	80.0	Same as above 49.3/50.7
G	* 4 1520	SA/PA 7/3	PO	2017	75.0	COOH/OH 48.0/52.0
H	* 5 4800	HA/PA 7/3	Same as above	5392	89.0	Same as above 30.0/70.0
I	* 6 3500	HA/TA/MA 6.4/1.6/2.0	EO	4040	86.6	Same as above 35.5/64.5

Notes:

*1 Organic dicarboxylic anhydride

*2 Epoxide

*3 α - ω -poly-1,2-butadiene glycol (Nisso PB-G1000 produced by Nippon Soda, Inc.).*4 α , ω -poly-1,2-butadiene dicarboxylic acid (Nisso PB-C1000 produced by Nippon Soda, Inc.).

*5 End carboxyl modified poly-1,4-butadiene (Hycar CTB produced by Ube Kosan, Inc.).

*6 End carboxyl modified poly-1,4-butadiene acrylonitrile block copolymer (Hycar CTB containing 8 mol % of acrylonitrile produced by Ube Kosan, Inc.).

SA: Succinic anhydride

5 PA: Phthalic anhydride

MA: Maleic anhydride

HA: Cyclohexane dicarboxylic anhydride

TA: Cyclohexane dicarboxylic anhydride

PO: Propylene oxide

10 EO: Ethylene oxide

15

20

25

30

35

40

45

50

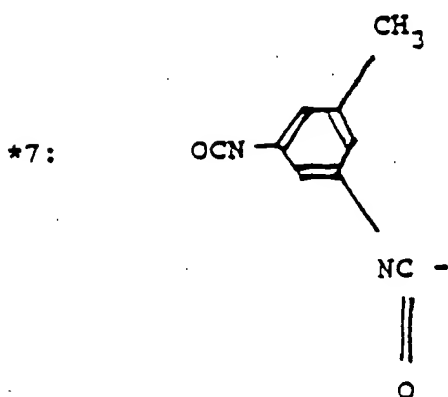
55

Test No.2 (End modified PD-PES block copolymers)

End modified PD-PES block copolymers were obtained from B' of Table 1a (except for K in Table 2a which was obtained from F' in Table 1a).

TABLE 2a

Kind	Modifying Agent	Structure of End Group
J	Succinic anhydride	-COOH
K	Same as above	-COOH
L	Glycidyl Methacrylate	$\text{CH}_2 = \underset{\text{CH}_3}{\underset{ }{\text{C}}} - \text{COO} -$
M	Toluilene di-isocyanate	* 7
N	Epichlorohydrine	$\text{CH}_2 - \underset{\text{O}}{\underset{ }{\text{CH}}} - \text{CH}_2 -$
O	Methylchloride	$\text{CH}_3\text{O}-, \text{CH}_3\text{O} \overset{\text{O}}{\parallel} \text{C} -$
P	Ca(OH) ₂	Calcium carboxylate

Note:

Evaluation No. 1

Placed in a beaker were 60 weight parts of a styrene solution of unsaturated resin containing 60% of solid component (polyset 9107 produced by Hitachi Kasei, Inc.: phthalic ester type), 27 weight parts of styrene monomer and 13 weight parts of an additive listed in Table 3a. After the mixture was made uniform and stirred by a propeller stirrer for 5 minutes, it was removed into a 100ml measuring cylinder and its phase separation (volume %) was measured over a period of time while left standing at room temperature. The results are show in Table 3.

TABLE 3a

<u>Additive</u>	<u>Condition Immediately After Resting Quietly</u>	<u>After 20 Minutes</u>	<u>After One Hours</u>	<u>After Six Hours</u>	<u>After 24 Hours</u>
A	White turbid dispersion	0	0.5	3	10
B	White turbid dispersion with small particles	0	0	1	3
C	Nearly soluble minute dispersion	0	0	0	0
D	Soluble Condition	0	0	0	0
E	Dissolved	0	0	0	0
PBG	Separation into two layers	12	12	13	13
SBS	White turbid dispersion - partial separation	5	12	13	14
SES	White turbid dispersion	2	10	12	13

Notes:

A - E: as in Table 1

PBG: α,ω -poly-1,2-butadiene glycol (Nisso PB-G1000 produced by Nippon Soda, Inc.)

SBS: Styrene-butadiene-styrene block copolymer (Califlex TR1102 produced by Shell Chemicals, Inc.)

SES: Styrene-type block copolymer obtained by suspension polymerization of end modified polyester with styrene monomer (Example No. 1 of Japanese Patent Publication Tokkai 60-99158).

Evaluation No. 2

Placed inside a Banbury mixer were 40 weight parts of 33% styrene solution of J in Table 2a, 60 weight parts of unsaturated polyester resin (Yupika 7507 produced by Nippon Yupika, Inc.), 1.5 weight parts of tertiary butyl perbenzoate and 3.0 weight parts of zinc stearate. To this was added 200 weight parts of calcium carbonate powder and after the mixture became homogeneous, 60 weight parts of glass fibres with fibre length 1/2 inch were added. One minute later, the mixer was stopped and the premix obtained was moulded at 145°C. Surface lustre was observed on the moulded sheet. Its shrinkage by moulding was 0.005%.

When the premix using PBG of Table 3a was substituted for J, the surface lustre of moulded sheet was extremely irregular.

Evaluation No. 3

Mixed together were 40 weight parts of 33% styrene solution of the additives listed in Table 4a, 60 weight parts of unsaturated polyester resin (Polyset 9120 produced by Hitachi Kasei, Inc.), 3 weight parts of zinc stearate, 1.5 weight parts of tertiary butyl perbenzoate, 140 weight parts of calcium carbonate powder and 0.3 weight parts of parabenzquinone. To this were added 2 weight parts of magnesium oxide and a composition containing 10% of glass fibres of length 1 inch was produced immediately. This was moulded into a mould and heated for moulding at mould temperature of 140°C to obtain an SMC. Its surface lustre was examined visually and its shrinkage rate was obtained. The results are shown in Table 4a.

TABLE 4a

Additive	Surface Lustre	Shrinkage Rate Upon Moulding (%)
A	b	-0.10
B	a-b	-0.07
C	a	-0.02
D	a	0.06
E	a	0.12
PBG	c	-0.20
PBA	c	-0.18
SES	b	0.25

Notes:

A - E, PBG, SES: As explained above.

PBA: α,ω -poly-1,2-butadiene dicarboxylic acid (Nisso PB-C1000 produced by Nippon Soda, Inc.

Evaluation: (a) = Good lustre
(b) = Not very good lustre
(c) = No lustre

Evaluation No. 4

Polybutylene terephthalate resin (relative viscosity of 0.5% orthochlorophenol solution at 25°C: 1.70) and additive of Table 5a were mixed at weight ratio of 90/10 and pellets were produced by melting and kneading by means of an extruder having a vent with diameter of 30mm. After the pellets obtained were dried under vacuum, moulded products were obtained by injection moulding. Izod impact strength (with notches) was measured (ASTM-D256-56) and the dispersion of additives in the matrix resin was observed with an electron microscope. The results are show in Table 5a.

When PBA was used with reference to Table 5a, there were free rotations of the extruder screw during the pellet-forming process caused by incomplete kneading and a small amount of coagulated PBA spilled out of the vent opening.

15

20

25

30

35

40

45

50

55

TABLE 5a

5			
10	<u>Additive</u>	<u>Izod Impact Strength</u>	<u>Dispersion Condition</u>
	A	7.9	Fine dispersion
15	B	8.4	Same as above
	C	8.2	Same as above
20	D	7.5	Extremely fine dispersion
	E	6.8	Extremely fine dispersion - completely compatible
25			
	PBA	2.5 - 3.2	Fine - bulk dispersion
30	SES	2.8	Fine dispersion
	None	3.0	-
35			

40 Notes:

45 A - E, PBA, SES: As explained above

50 Range regarding PBA indicates fluctuations, depending on the position.

Evaluation No. 5

55

The PD-PES block copolymers listed in Table 2a were measured and observed as explained above in connection with Evaluation No. 4 and comparisons were made with N of Table 1a. The results are shown in Table 6a. The added amount of additives was 12.5%.

TABLE 6a

5

	Additive	Izod Impact Strength	Dispersion Condition
	B	8.4	Fine dispersion
10	N	9.0	Same as above
	O	8.6	Same as above

15 As will be appreciated from the above Examples, the additives of the present invention include [liquid rubber]/[polyester] block copolymers which have the characteristics of both liquid rubber compounds and the polyester polymers and with affinity to both. They provide superior moulding workability, and products with superior surface quality, improved mechanical strength and reduced shrinkage may can be obtained.

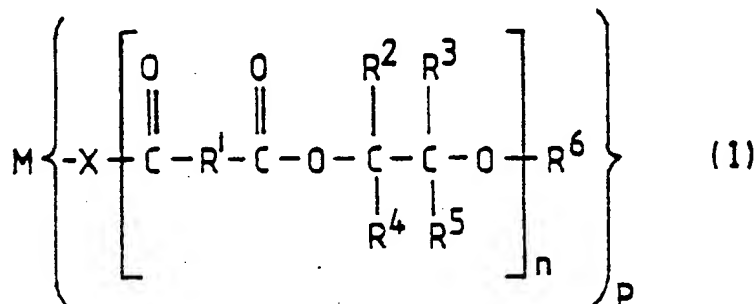
20

Claims

1. A block copolymer comprising a liquid rubber substituted with at least one polyester grouping, and functional derivatives thereof.
- 25 2. A block copolymer according to claim 1, wherein the polyester grouping is derived from reaction between a dicarboxylic anhydride and an epoxide.
3. A block copolymer according to either of claims 1 and 2, which has the formula (I)

30

35

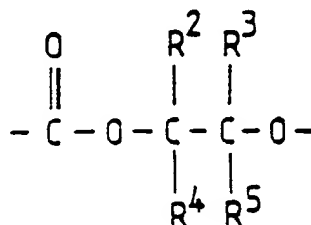


40

wherein M is substantially all or part of a molecule of a liquid rubber;
X is oxygen, sulphur, imino, amino, C₁₋₈ alkyl-substituted amino or the group

45

50



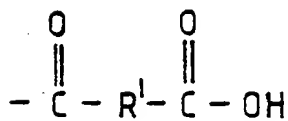
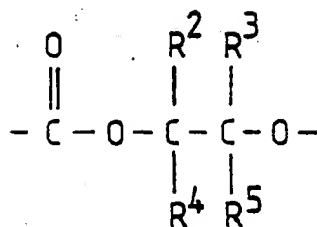
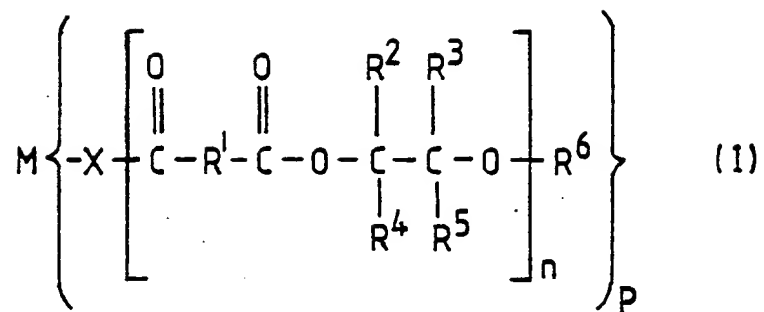
wherein R¹-R⁵ are as defined below;

- 55 R¹ is C₁₋₈ straight, branched or cyclo-alkylene or C₂₋₈ straight, branched or cyclo-alkenylene, optionally substituted by hydroxy, amino, C₁₋₄ alkyl, C₁₋₄ alkoxy or any combination thereof, or is a C₆₋₁₀ delocalised ring system, optionally substituted as above, and is the same or different in each repeat unit;
R²-R⁵ are the same or different and are hydrogen or C₁₋₄ alkyl and are the same or different in each repeat unit;

n and p are positive integers;
R^a is hydrogen or



- 5
- 10 wherein R¹ is as defined;
and functional derivatives thereof.
4. A block copolymer according to claim 3 wherein the liquid rubber is a polydiene.
5. A block copolymer according to claim 4 wherein the liquid rubber is a homopolymer of polybutadiene or polyisoprene.
- 15 6. A block copolymer according to any of the preceding claims wherein the functional derivatives are salts, esters or amides.
7. A block copolymer according to any of claims 3 to 6 wherein at least 2 of R²-R⁵ are hydrogen.
8. A block copolymer according to claim 7 wherein one of R²-R⁵ is hydrogen methyl or ethyl and the remainder are hydrogen.
- 20 9. A block copolymer according to any of claims 3 to 8 wherein R¹ is methylene, ethenylene, 1,2-dihydroxyethylene, benzylene, cyclohexylene, cyclohexenylene or cyclohexenylmethylene.
10. A block copolymer according to any of claims 3 to 9 wherein X is oxygen.
11. A block copolymer according to any of the preceding claims wherein the free ends of the polyester groupings are substituted with a vinyl, epoxy, isocyanate or amino group.
- 25 12. A block copolymer according to any of claims 1 to 10 wherein the ends of the polyester groups are blocked by an ester, ether, amide or methane group.
13. A block copolymer according to any of claims 1 to 10 wherein more than 25% the free ends of the polyester groups are carboxyl or hydroxyl.
14. A block copolymer according to any of claims 1 to 13 wherein the weight ratio of said liquid rubber: said polyester portions is between 5% and 95%.
- 30 15. A block copolymer according to claim 14 wherein the said ratio is between 40% and 90%.
16. An additive for synthetic resins comprising a block copolymer according to any of the preceding claims.
17. An additive according to claim 16 as dependant on claim 14 wherein the said ratio is between 10% and 95%.
- 35 18. A method of producing block copolymer according to claim 1, comprising reacting a liquid rubber having one or more reactive hydrogen atoms within its molecule with at least one organic dicarboxylic anhydride and one or more species of 1,2-epoxide in the presence of catalyst.
19. A method according to claim 18 wherein the said hydrogen atom is provided by a hydroxyl group or a carboxyl group.
- 40 20. A method according to either of claims 18 and 19 wherein the said catalyst is lithium halide or a tetra-C₁₋₄ alkyl ammonium salt.



THIS PAGE BLANK (USPTO)